

**CHANGES IN NUTRIENT DYNAMICS IN THE GULF OF MEXICO DUE  
TO INCREASE IN MISSISSIPPI RIVER FLOW**

An Undergraduate Thesis  
Presented to  
The Academic Faculty

by

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In Partial Fulfillment  
of the Requirements for the Degree  
Bachelor of Science in the  
School of Biology, College of Sciences

Georgia Institute of Technology  
December 2015

**CHANGES IN NUTRIENT DYNAMICS IN THE GULF OF MEXICO DUE  
TO INCREASE IN MISSISSIPPI RIVER FLOW**

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## **ABSTRACT**

The Gulf of Mexico underwent multiple environmental changes in 2010 and 2011, including the Deepwater Horizon oil spill and a large increase of freshwater input from the Mississippi River. Both of these events had the potential to change nutrient dynamics. In this study, I focused on the changes of nutrient dynamics in surface water in the northern Gulf of Mexico and what brought about those changes. It was found that surface water nutrient concentrations of nitrate, nitrite, and phosphate were much higher in the year 2011. This change was found to be due to the freshwater input from the Mississippi River through geographical location and relation to salinity.

# **CHAPTER 1**

## **INTRODUCTION**

The two nutrients that most commonly limit production in the ocean are nitrogen and phosphorous. The Redfield ratio is the ratio in which carbon, nitrogen, and phosphorous (106C:16N:1P) are present in the deep ocean (Weber and Deutsch 2010). Nitrogen is the key nutrient limiting primary production in most parts of the surface ocean. Dissolved inorganic nitrogen is not typically present in surface waters, the abundant dinitrogen that is present is only available to nitrogen fixers, or diazotrophs (Voss, Bange et al. 2013). Therefore, many studies are focused on the source of nitrogen in different areas of the ocean (Montoya 1996, Brandes 1998, Mandal 2012, Swart, Anderson et al. 2013).

### **Study Site: The Gulf of Mexico**

Estuaries and river plumes are of particular interest due to their variable freshwater and saltwater composition and the input of nitrogen from terrestrial sources. The Gulf of Mexico has many possible sources of nitrogen and other nutrients, including the Mississippi River, the Atlantic Ocean, and autochthonous organic matter. The natural abundance of the stable isotopes of nitrogen can help distinguish among sources of nitrogen (Montoya 2002), and in particular can show the importance of nitrogen fixation as a source of nitrogen to support life. Additionally, changes in the elemental ratio of nutrients and organic matter can provide information on how different nitrogen sources may affect the ecosystem. Past research on nitrogen isotopic ratios in the Gulf of Mexico has focused on phytoplankton and zooplankton (Holl 2007, Holl and Montoya 2008, Cai, Guo et al. 2012, Dorado, Rooker et al. 2012), and the isotopic composition of inorganic nitrogen in the Gulf is poorly known.

A combination of organic and inorganic samples will provide integrative information on the sources of nitrogen that support the Gulf of Mexico ecosystem.

## **Deepwater Horizon Oil Spill & Change in Mississippi River Flow Rate**

Studies of zooplankton and phytoplankton nutrient dynamics have to account for the quick turnover times of biological nitrogen; in contrast, dissolved inorganic nitrogen samples integrate over different time scales and depths and are inherently less dynamic. In this study, we explore the sources of nitrogen supporting production in different parts of the Gulf of Mexico as well as changes caused by the Deepwater Horizon oil spill in 2010 and high flow rate of the Mississippi River in 2011 due to flooding in the Midwest United States. I hypothesize that the high flow rate of the Mississippi River will significantly change the nutrient dynamics in the surface waters of the Gulf of Mexico due to introduction of nitrate and phosphate.

In addition to the large quantities of oil that accumulated at the surface, the Deepwater Horizon oil spill created a large deep water oil and gas plume at about 1100 m depth (Camilli 2010, Reddy, Arey et al. 2012). Though the oil did not contain significant quantities of nitrogen, it did add a large amount of  $^{13}\text{C}$ -depleted carbon to the water column. I hypothesize that this input of organic carbon led to N-limitation, which in turn promoted nitrogen fixation and drove a change in inorganic nutrient ratios leading to a positive  $\text{N}^*$  value. A positive  $\text{N}^*$  value would indicate that nitrogen is present in excess relative to the Redfield Ratio with phosphorus (Eq. 1). One month after the capping of the well, nitrogen fixation was found in the deep water surrounding the plume using the nitrogen fixation tracer assay from Montoya et al., (Montoya 1996), these data are as of yet unpublished. This finding shows a major shift from a system dominated by nitrate and other bio-available nitrogen sources and limited diazotroph activity to a system where diazotrophs were much more abundant.

## **CHAPTER 2**

### **LITERATURE REVIEW**

Nitrogen is the main limiting nutrient in surface waters of the world's oceans. Low levels of nitrogen can limit ecosystem productivity; high levels of nitrogen, on the other hand, can lead to an ecosystem where rapidly growing organisms bloom and use up other resources, such as oxygen, and may create an oxygen minimum or anoxic zone (Vitousek and Howarth 1991, Malakoff 1998).

The study of nitrogen flux into and out of the ocean can be conducted through isotopic analysis of zooplankton, phytoplankton, and dissolved inorganic nitrogen in the water column (Mariotti, Lancelot et al. 1984, Montoya 2009), but previous isotopic studies in the Gulf of Mexico have not extended to dissolved inorganic nitrogen. The addition of isotopic measurements of dissolved inorganic nitrogen in the Gulf of Mexico will provide a new perspective on sources and fluxes of nitrogen in the region.

Most studies of nitrogen supply to marine systems have focused on waters close to shore, often at river mouths or at the sources of agricultural run-off (Mandal 2012, Swart, Anderson et al. 2013). Fertilizer, legumes and pasture, and animal manure make up the majority of nitrogen input into the Mississippi Basin, which feeds into the Gulf of Mexico (Goolsby 2000). The input of this nitrogen into the Gulf of Mexico may also be dependent on flow rates of the Mississippi River.

River run-off is not the only important source of nitrogen entering the Gulf. Flow of water from the Atlantic Ocean, upwelling of deep water, as well as changes in system dynamics caused by anthropogenic input of carbon, can all provide nitrogen to surface waters in the Gulf of Mexico (Walsh, Dieterle et al. 1989, Reid 1994). Each of these sources has been investigated individually as well as in combination at times, but to date, isotopic studies have focused on only organic samples.

In addition to studies of nitrogen, the stoichiometry of the important marine nutrients carbon, nitrogen, and phosphorous provides important insight into oceanic processes (Anderson and Pondaven 2003, Arrigo 2005). The ratio of these nutrients in deep oceanic waters is typically 106 carbon atoms to 16 nitrogen atoms to 1 phosphorous atom (Weber and Deutsch 2010). Deviations from this ratio (Falkowski 1998) may reflect environmental changes; in the case of the Gulf of Mexico, changes in the contribution of the Mississippi River to the Gulf of Mexico and oil spills may both alter nutrient ratios (Lane, Day et al. 2004, Hu, Cai et al. 2014). These changes can in turn lead to large-scale hypoxia events, shifts in food chains, and harmful algal blooms.

The Deepwater Horizon oil spill is an example of a perturbation that changed nutrient dynamics in the Gulf of Mexico. The spill occurred at the MC252 Macondo well site at 1500 m below the sea surface and was the largest accidental release of oil to the ocean to date. This deep-water release led to a deep water oil and gas plume extending to the southwest at approximately 1100 m depth (Camilli 2010). The methane injected into the water column persisted for much longer than originally expected, occurring at levels greater than background 9 months after the wellhead was capped (Crespo-Medina, Meile et al. 2014). This large input of organic carbon may have perturbed both the carbon and the nitrogen cycles of the deep Gulf of Mexico.

## **CHAPTER 3**

### **METHODS**

Water samples were collected at a series of stations in the Northern Gulf of Mexico aboard the *R/V Oceanus* in the summer of 2010 (OC468; Fig. 1) and aboard the *R/V Endeavor* in the summers of 2011 (EN496; Fig. 2). Our sampling included waters around the Deepwater Horizon oil spill site as well as areas affected by natural oil and gas seeps.

#### **Sample Collection**

##### *Water Samples*

A CTD-rosette system was used to collect water samples for nutrient analysis, as well as measure temperature, salinity, oxygen concentration, and chlorophyll a concentration in the water column. The water samples were pressure filtered to collect suspended particles, then preserved by acidification and stored for analysis on shore. Sample depths extended from the surface to 2000 meters. This study focuses on samples that were collected in surface waters (0-5m). The stations examined were chosen based on the location of the Macondo wellhead of the Deepwater Horizon oil spill and the Mississippi River plume.

#### **Sample Analysis**

##### *Nutrients*

Nutrient concentrations were measured at sea using a Lachat QuikChem 8000 FIA nutrient analyzer. The system was calibrated using a concentration series of standards in deionized water. Saltwater standards were used in addition to freshwater standards to account for changes in light refraction due to the salt present in seawater.



### *Nitrite and Nitrate*

The nitrite in a sample is diazotized under acidic conditions with sulfanilamide. The diazonium ion created is then coupled with N-(1-naphthyl)ethylenediamine dihydrochloride, which was measured colorimetrically ( $\lambda = 520$  nm). Nitrate was reduced to nitrite for analysis by passage over copperized cadmium (QuikChem® Method 31-107-04-1-A).

### *Phosphate*

Phosphate in samples was reacted in an acidic environment with ammonium molybdate and antimony potassium to form antimony-phospho-molybdate complex, which was then reduced by ascorbic acid. The reduced compound is blue and was measured colorimetrically ( $\lambda = 880$  nm) (QuikChem® Method 31-115-01-1-I).

### *Suspended Particles*

Filters were pelletized in tin capsules for isotopic analysis by continuous-flow isotope ratio mass spectrometry using a Micromass Optima interfaced to a Carlo Erba NC2500 elemental analyzer. Each analytical run contained standards for both elemental (methionine) and isotopic (peptone) standards.

## CHAPTER 4

### RESULTS

#### Salinity

In 2010, the surface waters in the Gulf of Mexico ranged in salinity between 27.7 and 36.1 psu (Fig. 3a). In 2011, the surface waters ranged in salinity from 13.7 and 36.1 psu (Fig. 3b). The lowest salinities in both years were observed in proximity to the mouth of the Mississippi River between 28 and 29°N (Fig. 3a, b), with the minimum value in 2011 found at 28.58°N 89°W (Fig. 3b). Standard deviation of salinities in 2010 was  $\pm 1.7$ , whereas in 2011 it was  $\pm 5.4$ .

#### Nutrients

##### *Nitrite and Nitrate*

Surface water nitrite and nitrate was largely absent in 2010 (Fig. 4a). The highest value measured in 2010 was 0.7  $\mu\text{M}$ . In 2011, nitrite and nitrate was present in surface waters at much higher concentrations; the highest value measured was 31.3  $\mu\text{M}$  located in the low salinity area created by Mississippi River input at 28.58°N 89°W (Fig. 4b, Fig 8b).

##### *Phosphate*

Similarly to nitrite and nitrate, surface water phosphate was largely absent in 2010 with a maximum value of 0.19  $\mu\text{M}$  (Fig. 5a). In 2011, phosphate was present in higher concentrations in these surface waters with the highest value measured 0.996  $\mu\text{M}$  (Fig. 5b). As in the case of nitrite and nitrate, the highest concentrations were present in the areas of lowest salinity (Fig. 7b).

### *C:N Ratio*

In 2010 and 2011, areas of low ( $< 6.6$ ) and high ( $> 6.6$ ) C:N ratios were present in the Gulf of Mexico (Fig. 6a, b). C:N ratios did not align with salinity or nutrient concentration patterns. The minimum C:N ratio recorded in 2010 was 5.45 at  $29^{\circ}\text{N}$   $89.79^{\circ}\text{W}$  (Fig. 6a), and in 2011 was 5.32 at  $28.1^{\circ}\text{N}$   $87.1^{\circ}\text{W}$  (Fig. 6b). The maximum C:N ratio recorded in 2010 was 9.03 at  $28.6^{\circ}\text{N}$   $87.9^{\circ}\text{W}$  (Fig. 6a), and in 2011 was 10.65 at  $27.5^{\circ}\text{N}$   $88.95^{\circ}\text{W}$  (Fig. 6b).

### *N\* Fields*

In 2010, all  $\text{N}^*$  values were positive with a maximum value of 2.92 at  $28.8^{\circ}\text{N}$   $88.10^{\circ}\text{W}$  and minimum value of 0.19 at  $28.8^{\circ}\text{N}$   $88.08^{\circ}\text{W}$  (Fig. 9a) which does not align with salinity trends (Fig 3a).

In 2011, both positive and negative  $\text{N}^*$  values were recorded. The highest values aligned with the areas of lowest salinity (Fig. 3b, 9b), with the maximum  $\text{N}^*$  value 15.89 aligning with the minimum salinity value (13.6 psu) at  $28.58^{\circ}\text{N}$   $89^{\circ}\text{W}$ . The minimum  $\text{N}^*$  value was -8.33 at  $27.96^{\circ}\text{N}$   $88.13^{\circ}\text{W}$  (Fig. 9b).

## CHAPTER 5

### DISCUSSION

The Gulf of Mexico has been the focus of many research studies due to the Deepwater Horizon oil spill and due to its importance to the economy due to its tourism, oil drilling, and fisheries. This study provides an analysis of the nutrient changes due to the change in the flow rate of the Mississippi River that occurred between the year 2010 and 2011 through the integration of particle and dissolved inorganic nutrient data.

We documented a significant change ( $p < 0.05$ ) in the surface water salinity in the Gulf of Mexico between the years 2010 and 2011 (Fig. 3). This change in salinity was accompanied by a significant change in dissolved inorganic nitrogen ( $p < 0.05$ ; Fig. 4) and phosphorous ( $p < 0.001$ ; Fig. 5) concentrations as hypothesized.

The unusually high nutrient concentrations in the year 2011 was shown to be due to the changes in the Mississippi River flow rate, and not another source such as the Deepwater Horizon oil spill, through the relationship between higher nutrient ( $\text{NO}_3^- + \text{NO}_2^-$  and  $\text{PO}_4^{3-}$ ) concentration and lower salinities (Fig. 7b, 8b) and geographical orientation of the nutrient anomalies near the mouth of the Mississippi River (Fig. 3b).

The changes in the C:N ratio between 2010 and 2011 were not statistically significant ( $p = 0.364$ ). The values below the C:N Redfield ratio of 106:16 (6.6) show, that in many locations in the Gulf of Mexico, nitrogen is abundant it is not the factor limiting productivity (Fig. 6). The values that were above the C:N Redfield ratio indicate that the surface waters were being nitrogen limited (Fig. 6).

The  $N^*$  values, representing the ratio of N:P, were not significantly different between 2010 and 2011 ( $p = 0.264$ ). Though the maxima and minima values were extreme in 2011, the mean  $N^*$  value remained positive and aligned with the hypothesis that input of organic carbon

led to N-limitation, which in turn promoted nitrogen fixation and drove a change in inorganic nutrient ratios.

Future work should integrate deepwater samples into the analysis of the effects of the Deepwater Horizon oil spill and the high flow rate of the Mississippi River. The remineralization of the high concentrations of nutrients introduced into the Gulf of Mexico by the Mississippi River in 2011 should also be investigated.

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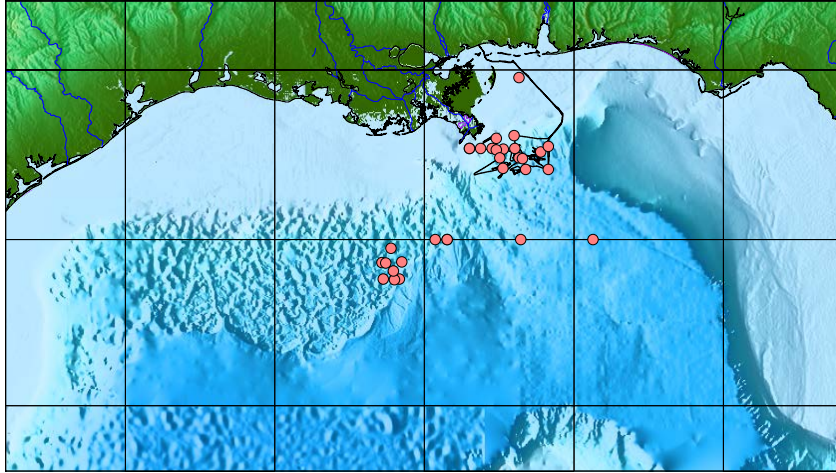
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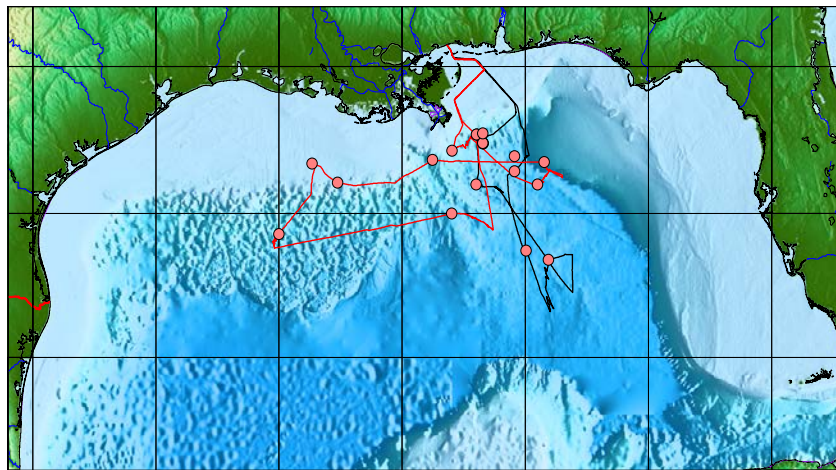
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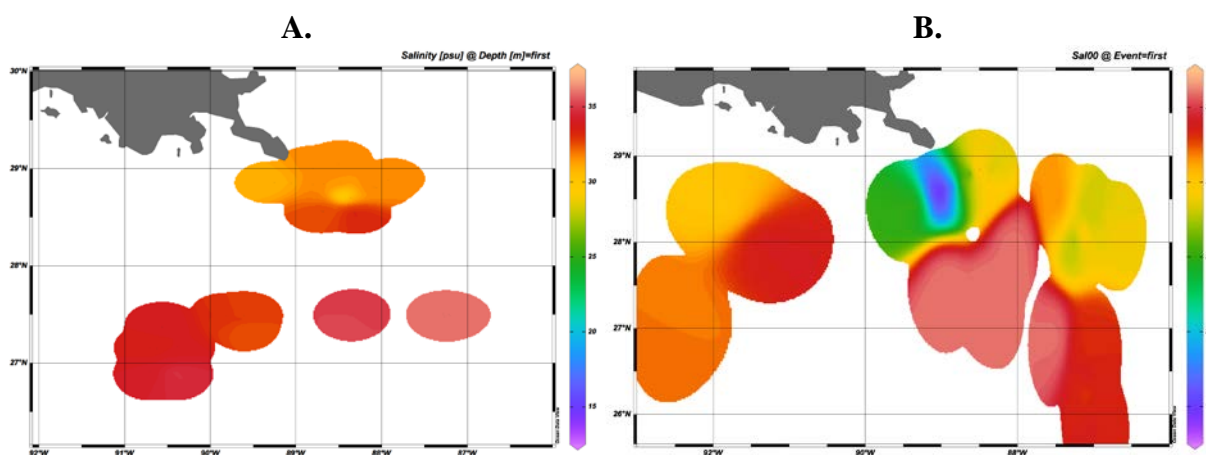
## FIGURES



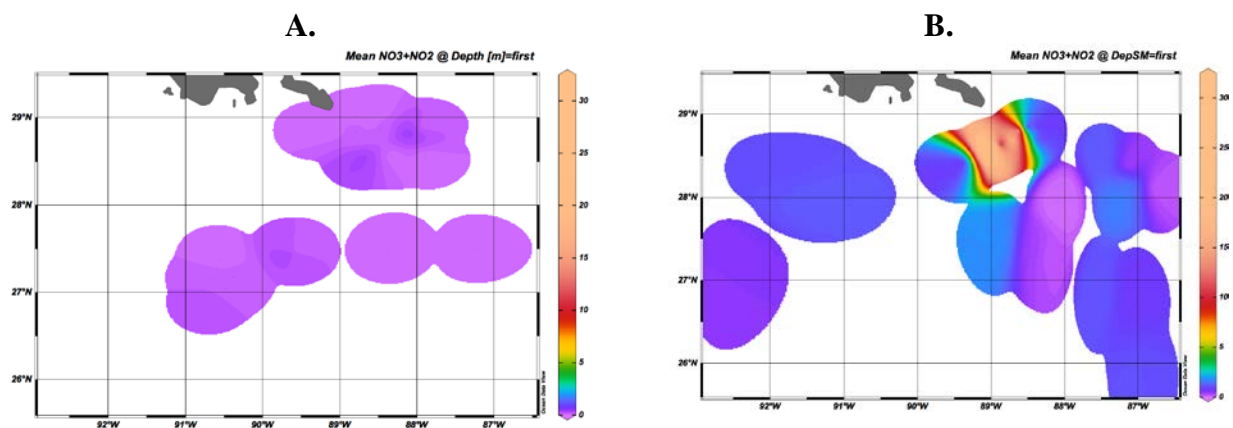
**Figure 1.** Cruise track of *R/V Oceanus* cruise OC468 in summer of 2010 in the northern Gulf of Mexico.



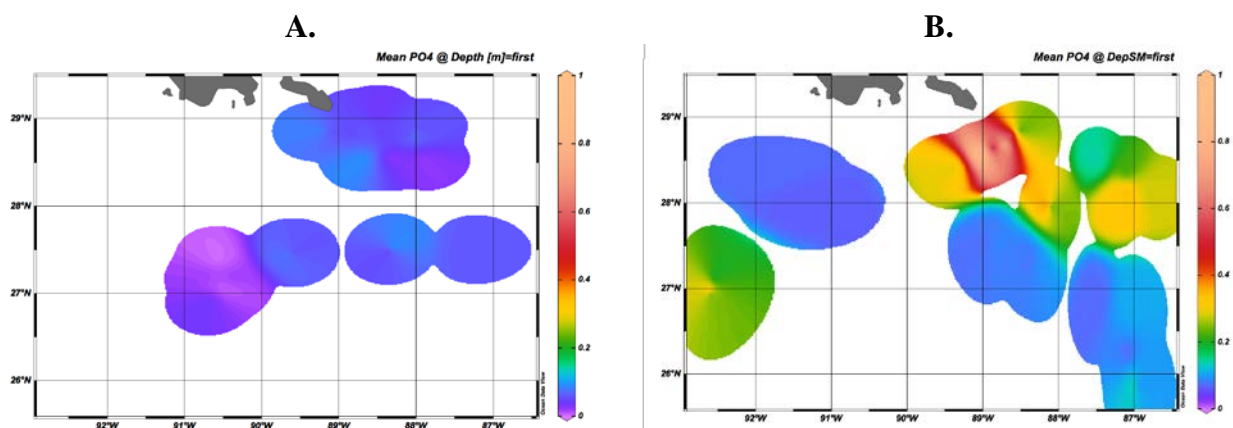
**Figure 2.** Cruise track of *R/V Endeavor* cruise EN496 in summer of 2011 in the northern Gulf of Mexico.



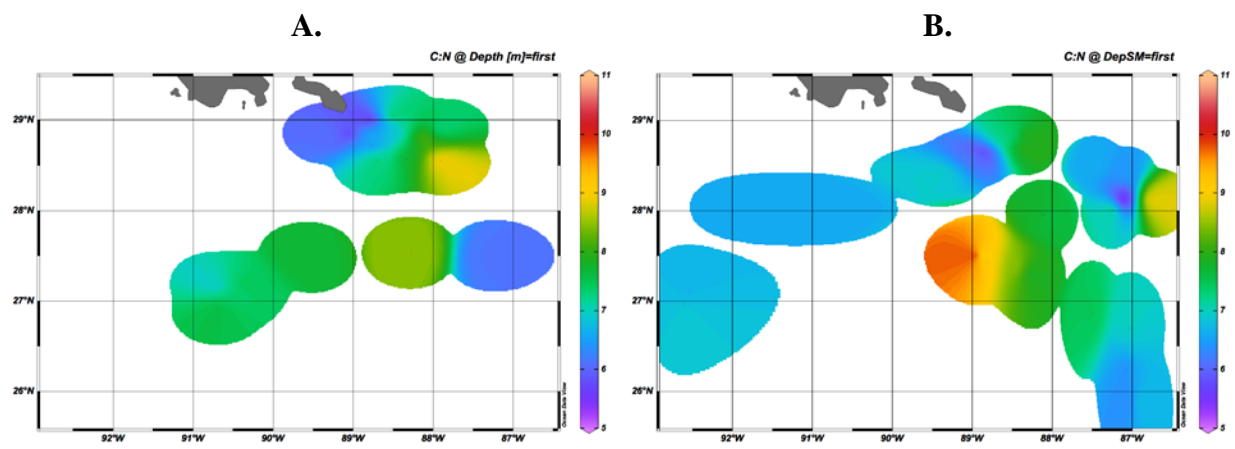
**Figure 3.** Surface distribution of salinity from cruise OC468 in 2010 (a) scaled to compare with salinity [psu] distribution from cruise EN496 in 2011 (b).



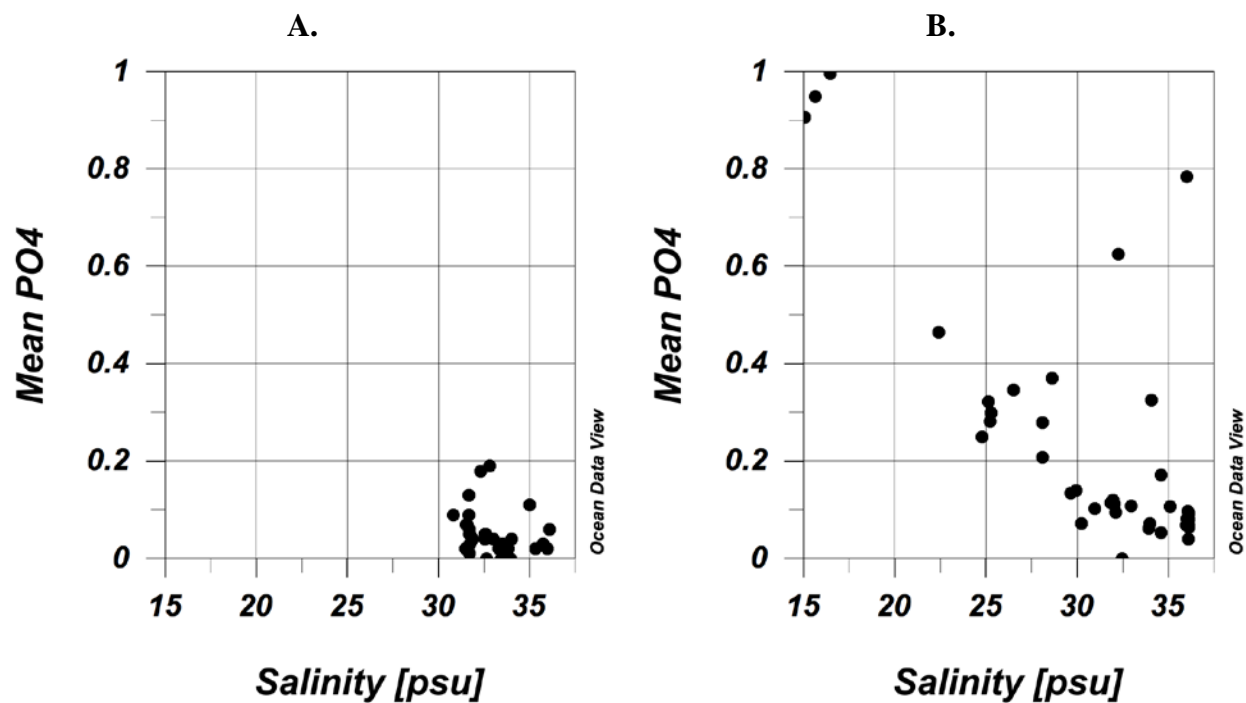
**Figure 4.** Surface distribution of nitrate and nitrite ( $\text{NO}_3^- + \text{NO}_2^-$ ) concentration [ $\mu\text{M}$ ] from cruise OC468 in 2010 (a) scaled to compare with concentrations from cruise EN496 in 2011 (b).



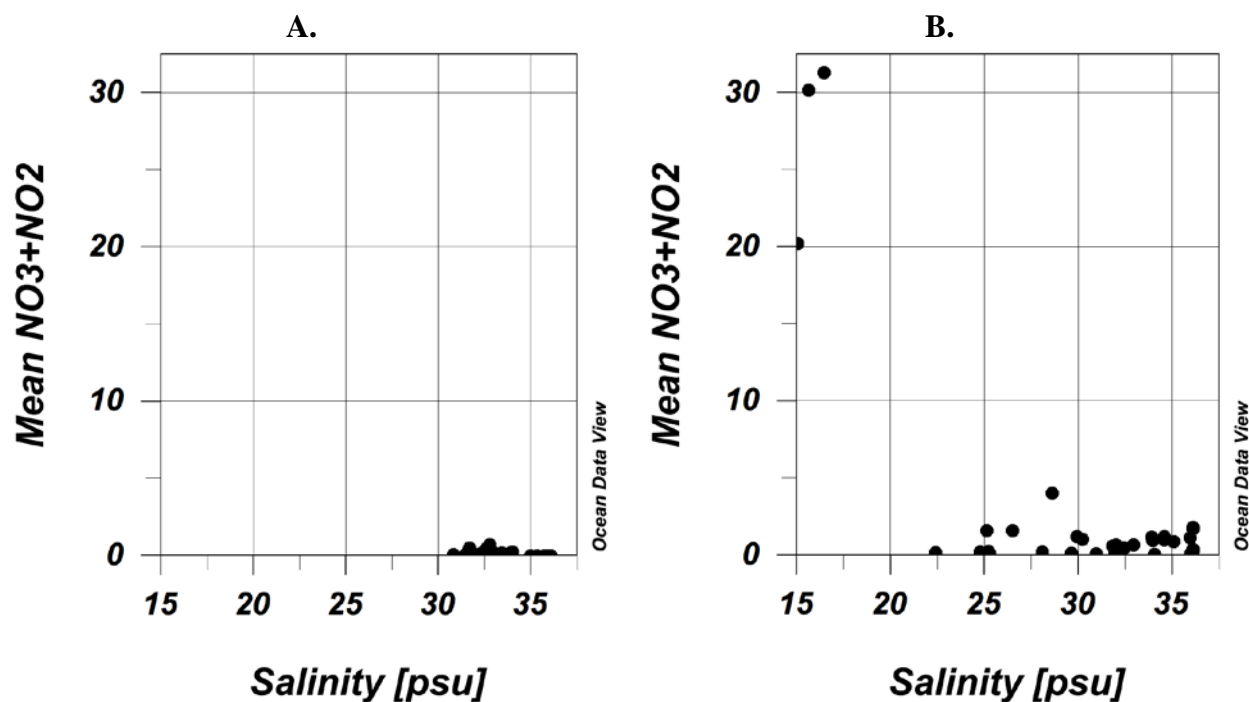
**Figure 5.** Surface distribution of phosphate ( $\text{PO}_4^{3-}$ ) concentration [ $\mu\text{M}$ ] from cruise OC468 in 2010 (a) scaled to compare with concentrations from cruise EN496 in 2011 (b).



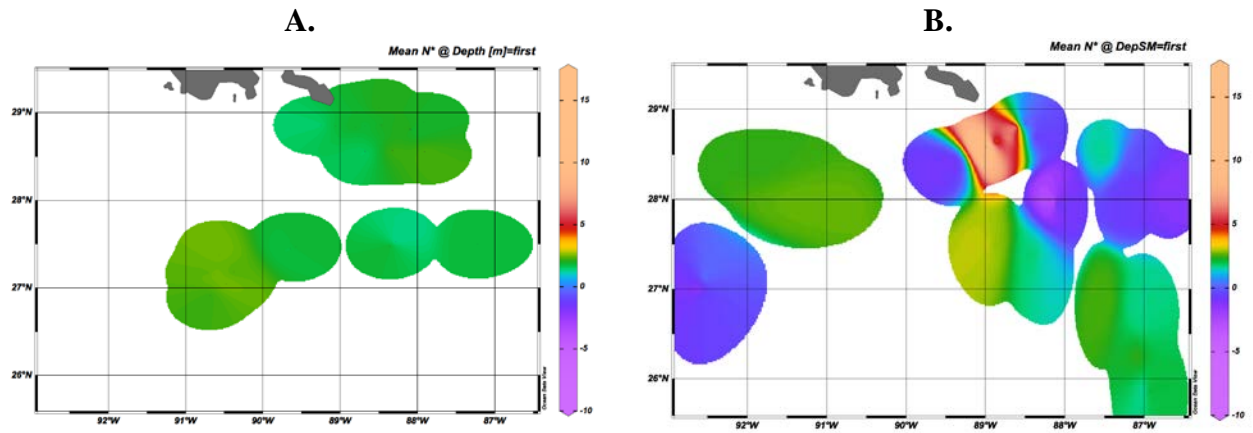
**Figure 6.** Surface distributions of C:N ratios from cruise OC468 in 2010 (a) and EN496 in 2011 (b).



**Figure 7.** Concentrations [ $\mu\text{M}$ ] of phosphate ( $\text{PO}_4^{3-}$ ) as a function of salinity [psu] from cruise OC468 in 2010 (a) and EN496 in 2011 (b).



**Figure 8.** Concentrations [ $\mu\text{M}$ ] of nitrate and nitrite ( $\text{NO}_3^- + \text{NO}_2^-$ ) as a function of salinity [psu] from cruise OC468 in 2010 (a) and EN496 in 2011 (b).



**Figure 9.** Surface distribution of  $N^*$  values from cruise OC468 in 2010 (a) scaled to compare with values from cruise EN496 in 2011 (b).

## APPENDIX

Equation 1:

$$N^* = ([NO_2^- + NO_3^-] - (16 \times [PO_4^{3-}]) + 2.9) \times 0.87$$